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RECOVERY OF GOLD FROM THIOUREA SOLUTIONS: INVESTIGATION OF CEMENTATION WITH METAL POWDER, ACTIVATED CARBON, ION EXCHANGERS AND SOLVENT EXTRACTION - PROGRESS REPORT

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RECOVERY OF GOLD FROM THIOUREA SOLUTIONS: INVESTIGATION OF CEMENTATION WITH METAL POWDER, ACTIVATED CARBON, ION EXCHANGERS AND SOLVENT EXTRACTION - PROGRESS REPORT

by

G. Deschênes*, P.J. Prud'hommet and E.W. Wongt

ABSTRACT

This progress report shows the actual results obtained for gold recovery from thiourea solutions. Cementation with aluminum and lead powders, adsorption with activated carbon, ion exchange with strong acid cationic resins and solvent extraction have been studied.

Cementation with aluminum powder is efficient and high extraction is provided (98%). However, quality of aluminum cement is poor. Cementation with lead powder is totally inefficient. Activated carbon extracts almost all gold (99%) but performance is overshadowed by a high loss of thiourea during carbon loading. Strong acid cationic resins provide high and selective extraction of gold but elution with thiourea liquor has not been successful to date. However, elution of the ion exchanger with a thiosulphate solution was interesting providing 97% gold stripping in preliminary tests. Solvent extraction of gold was selectively realized with a mixture of di-2-ethyl hexyl phosphonic acid and tributyl-phosphate. Stripping of the organic to recover gold is easily achieved in hydrochloric solution with 98% of the gold stripped.

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Récupération de l'or des solutions de thiourée: étude de la cémentation par poudre métallique, du charbon activé, des résines cationiques fortes et de l'extraction par solvant

par

G. Deschênes*, P.J. Prud'hommet and E.W. Wongt

RÉSUMÉ

Ce rapport partiel présente les résultats obtenus jusqu'ici sur la récupération de l'or des solutions de thiourée. La cémentation métallique avec des poudres d'aluminium et des poudres de plomb, l'adsorption par charbon activé, l'échange ionique avec des résines cationiques fortes et l'extraction par solvent ont été étudiés.

La cémentation avec une poudre d'aluminium est efficace et donne une extraction élevée (98%) contrairement à la poudre de plomb qui s'est révélée inefficace. La qualité du cément d'aluminium est cependant faible. Le charbon activé récupère pratiquement tout l'or (99%) mais il occasionne une perte importante de thiourée en adsorbant celle-ci et son utilisation nécessite certaines précautions. Les résines cationiques fortes extraient l'or sélectivement mais leur élution est assez difficile. Une solution de thiosulfate s'est montrée l'éluant le plus efficace avec une élution de 97% dans les essais préliminaires. Un mélange de di-2-ethyl hexyl phosphoric acid et de tributylphosphate permet une extraction sélective de l'or. Le recouvrement du métal précieux contenu dans l'organique se réalise facilement avec une solution d'acide chlorhydrique.

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1. INTRODUCTION

Cyanide leaching is largely used all over the world to extract gold from ores. The development of new processes and techniques could increase the possibility for recovery of gold from refractory materials. These methods include roasting, oxidative leaching, bioleaching, pressure leaching, and the use of thiosulfate and thiourea as lixiviants.

All industries have to take sufficient precautions for environmental protection. Hydrometallurgical operations in the mineral industry are concerned with potential seepage of reagents from large tailings ponds. More specifically, EPA (USA) forces industries to provide options in non-pollution methods for gold leaching. Thiourea leaching is one of the more promising approaches in these new techniques. Strict regulations in water quality will be the reason of gradual replacement of toxic processing, such as cyanidation, by less toxic technology.

Leaching with thiourea has been successfully tested on different materials (1-6). Commercial application in the extraction of gold and silver is performed in some areas (7-9) or plan to do so (10). Various techniques to recover gold and silver from this solution have been investigated. Cementation with aluminum (1,8,11), lead and iron (12,13,15, 16), activated carbon (2,4,7,13), ion exchange (2,11,13,14,17,18) and electrowinning (11,19-24) are the main avenues explored.

This progress report presents results of tests using cementation, activated carbon, ion exchange resins and solvent extraction to recover gold from thiourea solution.

2. MATERIAL, EQUIPMENT AND PROCEDURES

THIOUREA SOLUTION

Experimental solution was prepared by leaching Campbell Red Lake gold concentrate. Composition of the gold concentrate, leaching conditions and composition of the leach liquor are listed in Tables 1, 2 and 3.

Table 1. Analysis of the Campbell Red Lake gold concentrate

Element	Analysis
Au	307 g/t
Ag	43 g/t
Fe	24.8 %
S	18.3 %
SiO_2	29.3 %
As	9.8 %
Ca	1.6 %
Al	1.0 %
C	0.8 %
Sb	0.2 %
Cu	0.1 %

Table 2. Leaching conditions

Initial thiourea concentration	10.0 g/L
Initial $Fe_2(SO_4)_3$ concentration	5.0 g/L
Temperature	room
Pulp density (w/w)	30%
Stirring speed	800 rpm
pH control	1.0
Leaching time	60 minutes

Table 3. Analysis of the leach liquor

Element	Analysis
Thiourea	7.6-8.9 g/L
Au	31-43 mg/L
Ag	1 mg/L
Fe	8.2-9.4 g/L
As	1.2-2.4 g/L
Cu	22-43 mg/L
Sb	19-45 mg/L

Reagent grade chemicals and distilled water were used in experimental tests. Thiourea analysis was performed by mercuric nitrate titration or potentiometric titration with potassium iodate. Metal ion analyses were performed by atomic adsorption spectroscopy (AAS). Gold was also analysed by AAS or by inductively coupled plasma (ICP) at low concentrations ($\leq$1 mg/L).

3. CEMENTATION

EQUIPMENT AND PROCEDURE

Metal cementation was performed in 250-mL reactors. Agitation of the system was provided by a mechanical stirrer set at 340 rpm and temperature control by a thermobath (Thermomix 1480, Braun).

Metallic powders used were 100% -38 µm. Aluminum powder was obtained from Anachemia and lead powder by Fisher.

Extraction of gold was evaluated by analysis of solutions with atomic absorption spertroscopy or with ICP.

RESULTS AND DISCUSSION

Table 4 shows the extraction of gold with aluminum powder at room temperature. Tests 1 and 2 represent cementation with crude powder and powder washed with 0.2% caustic soda for 40-minute tests. There is some improvement in the gold recovery i.e. ~6%. If we increase the cementation time as presented in Test 3, the recovery of gold reaches 79% after 120 minutes. No thiourea loss was detected during these tests according to titration analysis.

Table 4. Cementation of gold with aluminum powder at room temperature. 500 mg Al/L, feed: 32 mg Au/L

Test No.	Cementation (min)	Gold Extraction (%)	Remark
1	40	9.1	Crude powder
2	40	15.2	Washed powder
3	120	78.8	Washed powder

Aluminum consumption was 18.9 kg/kg Au with 79% gold recovery.

Figure 1 shows the effect of aluminum powder concentration at 60°C with 40 minutes contact time. Gold recovery is 90.1% with 500 mg Al/L powder and 90.4% recovery is obtained if this concentration is increased to 750 mg/L. Aluminum powder requirement is 10.7 kg/kg gold at 71.9% recovery and increases to 20.7 kg/kg gold at 90.1% recovery. Pretreatment of the aluminum powder with caustic soda does not improve the gold recovery at this temperature. Arsenic, copper and antimony were respectively cemented at 3%, 57% and 40% with 500 mg Al/L. No thiourea loss was observed.

Figure 2 presents the effect of contact time with different concentrations of aluminum powder. Maximum gold recovery is 98.1% with 750 mg Al/L powder after 120 minutes of contact. Increasing the aluminum concentration to 1000 mg/L does not significantly improve the recovery.

Tests done with lead powder at -38 µm show that cementation with such a fine powder does not yield good recovery of gold. In fact, no gold recovery was possible with this powder, even with increasing the temperature to 60°C. The lead sulphate coating on particles was strong enough to prevent any gold deposition. The strength of the passivation coating decreases with the decrease of the contact surface. Lakefield Research (3) found that with lead shot 76% of gold was recovered in 4 hours. Then deposition of gold is only possible if microfissues occur at the surface of metal and it occurs with elements that have a large surface area such as lead shot and lead foil.

In our case, aqueous media is responsible for the bad performance of lead powder. Fine powder was successfully used in hydrochloric media (15). Gold was all extracted with a lead requirement of 7.5 kg/kg gold, however activity of the sulphuric acid and the stability of lead sulphate result in a poor performance of lead concentration in a sulphuric media.

Performance obtained with aluminum cementation is comparable with previous work (1,11); providing gold recovery of 98.1%. Final cement has a gold content equivalent to the one mentioned by Van Lierde, i.e. 2%. Higher precious metals content in the cement can be obtained when there is high silver concentration in solution, resulting in a lower requirement of aluminum powder (8-11).

Tests have shown that zinc powder is not viable for such solutions because of the high hydrogen evolution and consequently the large acid consumption and also the formation of arsine.

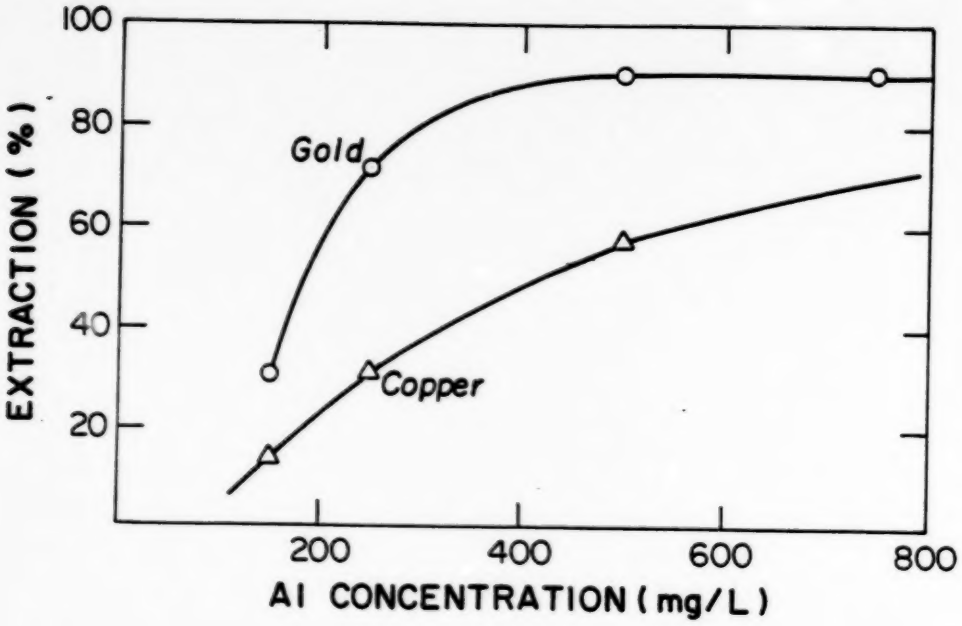

Fig. 1. Effect of aluminum concentration on gold recovery. Aluminum powder 100% -38 µm, 60°C, 40 minutes. Feed: 32 mg Au/L, 40 mg Cu/L.

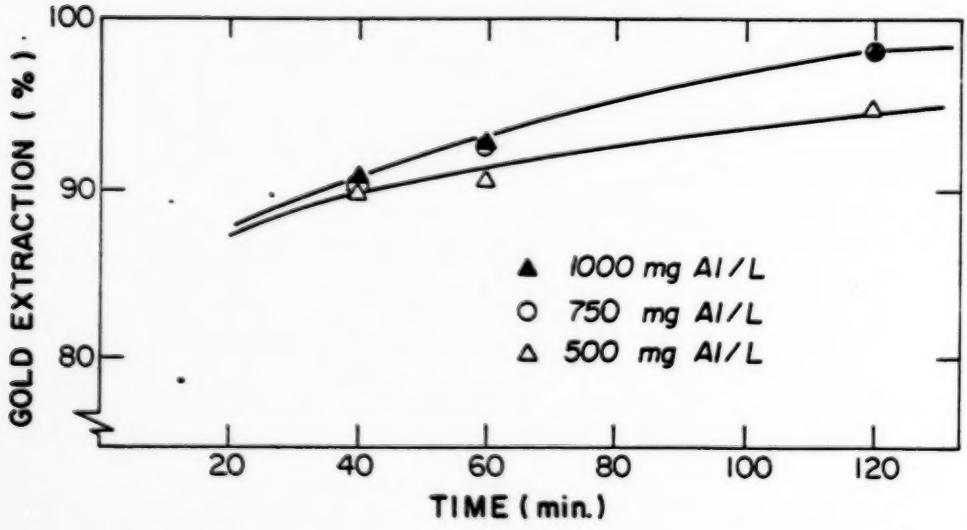

Fig. 2. Effect of time on gold recovery with cementation. Aluminum powder 100% -38 µm, 60°C. Feed: 32 mg Au/L.

Gold refining of a lead cement is more attractive than treating aluminum cement using pyrometallurgy. Unfortunately, fine lead powder is not practical in sulfuric solutions. The decrease in gold content by using lead shot or lead render is thus not economical.

The relatively low gold content in aluminum cement is also a problem and the refining of such a cement becomes uneconomical. Increasing gold content or decreasing the aluminum consumption are the keys to the successful application of this practice. A good example is the aluminum cementation applied to silver recovery with success (5). In such solutions, silver content is higher than the usual concentrations encountered in gold solutions. Aluminum requirement is thus reduced.

However, we have to keep in mind the eventual arsine formation when there is some arsenic in a solution. This is especially true in acidic solution during hydrogen evolution. The practice of cementation with metal must be established with care and with the appropriate systems.

4. ACTIVATED CARBON

EQUIPMENT AND PROCEDURE

Norit activated coconut shell carbon was used in these tests. Carbon conditioning was performed by wet screening on 850 µm screen and reactivation by heating at 700°C for two hours. After being quenched and filtrated, the activated carbon was kept in a closed container for use in adsorption tests.

Carbon loading was carried out in an incubator shaker at 500 rpm and leach solution (100 mL) was contacted with different amounts of activated carbon (0.5, 2.0, 3.0 and 5.0 g) during different shaking times (15-60 minutes). Analysis of the solution was performed by AAS after filtration of the pulp at the end of each test.

RESULTS AND DISCUSSION

Figure 3 shows that 99% of gold can be recovered with 50 g/L of activated carbon in 30 minutes. Extending the contact time to 60 minutes slightly improves the performance (~0.2%). The decrease of carbon concentration causes a drop in recovery. In fact, 30, 20 and 5 g/L of

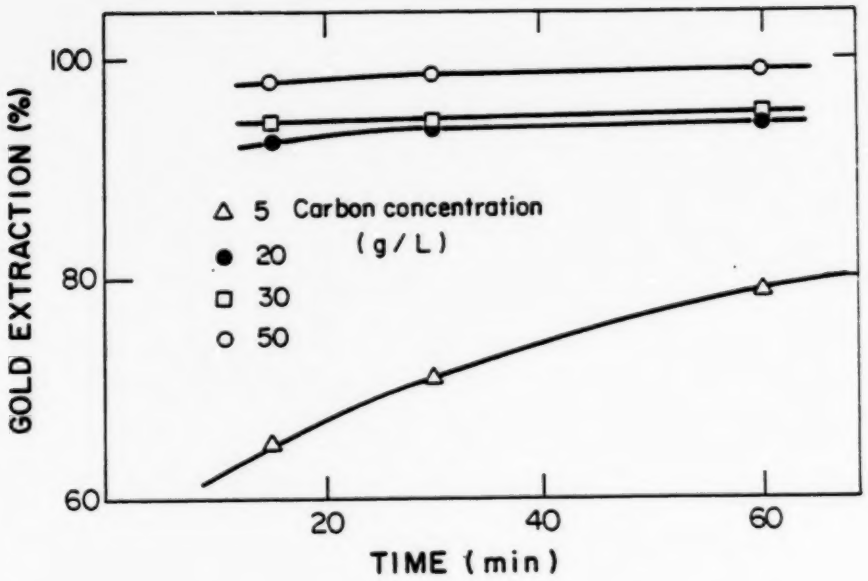

Fig. 3. Influence of carbon concentration on the gold recovery. Feed: 33 mg Au/L, room temperature.

activated carbon gave respective gold extraction of 95%, 94% and 79% after 60 minutes. High content of iron and arsenic in solution has resulted in high loading onto carbon. They have been loaded up to 170 kg/t and 120 kg/t respectively at 0.5 g carbon/L solution. Such loadings of competing ions result in a drop in the activated carbon efficiency for gold.

Figure 4 shows that carbon loading increases with a decrease of gold extraction. In this case, a loading of 5.4 kg Au/t was loaded in 60 minutes with 5 g/L of carbon resulting in the lowest recovery (79%) but giving the maximum loading. Recovery of 99% of gold was obtained but with the lowest loading of 0.72 kg Au/t (50 g/L of carbon).

Thiourea adsorption onto activated carbon is presented in Fig. 5. Extraction of thiourea increases with the concentration of activated carbon in a parabolic mode. With 50 g/L of carbon, 66% of thiourea was adsorbed

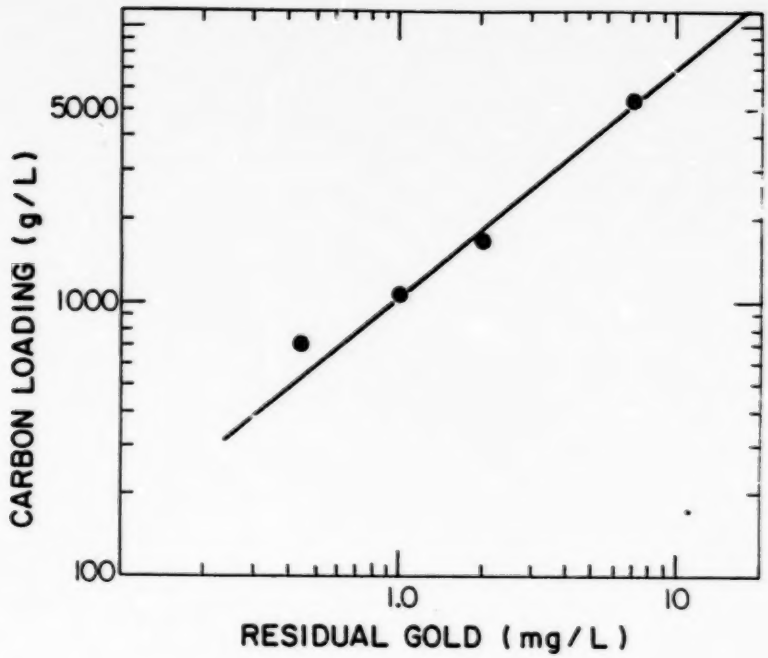

Fig. 4. Carbon loading with 60 minutes contact. Room temperature, feed: 32 mg Au/L.

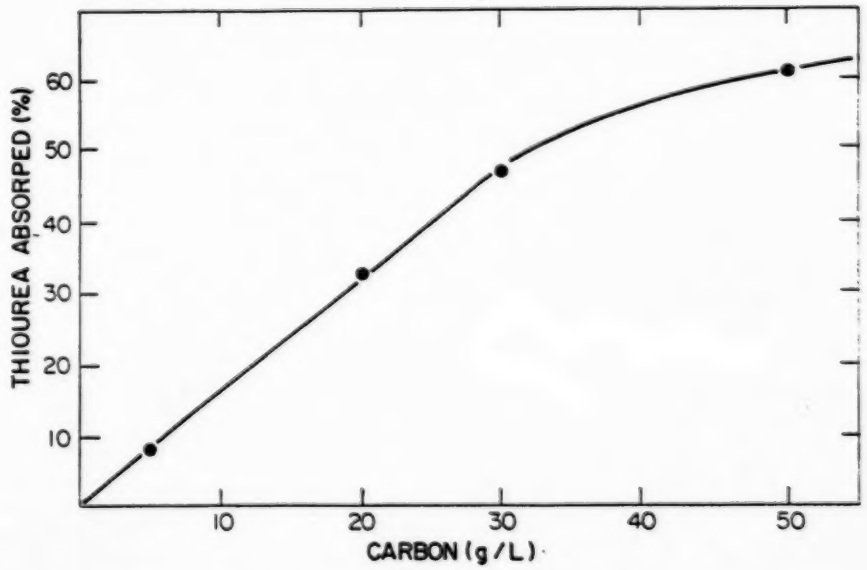

Fig. 5. Effect of activated carbon concentration on thiourea extraction from thiourea solution. Feed: 8.2 g/L thiourea, room temperature, 60 minutes contact.

in 60 minutes. These results confirm the results of Gabra (2) and Yen (13) and are totally opposed to Moussoulos' results that indicated thiourea was not adsorbed by activated carbon (4).

Table 5 presents elution tests to see if it is possible to recover thiourea from activated carbon loaded. An amount of 6.4 g of activated carbon loaded (11% thiourea) was contacted in a flask with 50 cc of solution for 60 minutes and stirred at 500 rpm.

Table 5. Elution of activated carbon to recover thiourea.

Eluant	Concentration of thiourea (g/L)	Thiourea elution (%)
Warmed water (40°C)	0.10	2.0
H_2SO_4, pH = 2.0	0.10	2.0
H_2SO_4, pH = 0	0.40	7.8
H_2SO_4, pH = -1.0	0.53	10.4

Thiourea is not easily eluted from this material with warmed water or even with acidic solution of H_2SO_4 at pH -1.0 (-50% V) at ambiant atmosphere. In fact, maximum elution of 10.4% was obtained with a solution of H_2SO_4 at pH -1.0.

It is quite possible that oxygen is responsible for the difficulty to recover thiourea. Schulze (14) said that it is possible to recover pure and concentrated thiourea solutions with a hot-water wash but this procedure must be performed under absence of oxygen to avoid thiourea decomposition on carbon. It is reported that when activated carbon reaches saturation with thiourea, no further adsorption occurred (13). This organic loading onto activated carbon represents a disadvantage and also affects the performance of the material in its gold loading. Although activated carbon can provide high loadings of gold (100 kg/t), competing ions like iron, copper and arsenic are also easily loaded onto this material. The prior removal of such elements would be required during the reactivation of the activated carbon, providing at least an additional step in the treatment. The special equipment required to get an efficient recovery of the leaching reagent

(thiourea) adsorbed onto activated carbon and the lack of selectivity during the adsorption cycle render the process less attractive. Further work was then oriented to other methods that could offer a simple, easy and economical step to recover gold.

5 RESINS

EQUIPMENT AND PROCEDURE

Eight resins were examined in this investigation. Table 6 shows technical information about the materials.

Batch and column adsorption tests were performed on the as-received resins. Batch tests were run by contacting 15 mL of resin with 150 mL of solution in 250 mL flasks agitated with incubator shaker (orbital) for 60 minutes at 500 rpm and 25-27°C. Solution was filtered and analysed at the end of each experiment. The ion-exchange column set-up is shown in Fig. 6. Gold thiourea solution was pumped through a specific volume of wet-settled resin after being filtered to avoid any particles in the system. The volume of resin used was in the range of 2 mL-10 mL. The resin bed has been supported and retained by glass wool.

Volumes of effluents were collected in graduated glass cylinders and analysed. The loadings of resins were evaluated by difference in head and effluent analysis. Fire assay was conducted on the resin occasionally to check the results. Batch elution of resins was conducted with the same apparatus used in loading. Fifteen mL of loaded resin were contacted with 50 mL of various eluants during 120 minutes at room temperature. In some occasions a second contact was provided.

RESULTS AND DISCUSSION

Loading

Table 7 shows batch tests loading results obtained for 7 resins. With a ratio of 1/10 (volume of resin/volume of aqueous), all gold extractions were over 90%, i.e. 94% to 99%. The exchange mechanism involved is:

$$\bar{X}^{+} + Au[SC(NH_2)_2]_2^{+} \rightleftharpoons X^{+} + \overline{Au[SC(NH_2)_2]_2}^{+}$$

Table 6. Details on the resins used for the recovery of gold from thiourea solution.

Resin	Manufacturer	Type	Ionic form	Active group	Matrix	Standard mesh distribution
HCR-S	Dow Chemical	SAC*	Na^+	sulphonic	styrene-DVB	20-50
50WX8	Dow Chemical	SAC	Na^+	sulphonic	styrene-DVB	20-50
MSC-1	Dow Chemical	SAC	Na^+	sulphonic	styrene-DVB	20-50
TG 650C	Dow Chemical	SAC	H^+	sulphonic	styrene-DVB	22-32
AG50W-X8	Bio-Rad	SAC	H^+	sulphonic	polystyrene	100-200
AG50W-X16	Bio-Rad	SAC	H^+	sulphonic	styrene-DVB	200-400
Lewatit OC1014	Bayer	unknown†	-	containing N and S	polystyrene	12-48

*strong acid cationic: SAC
†thiourea in the resin

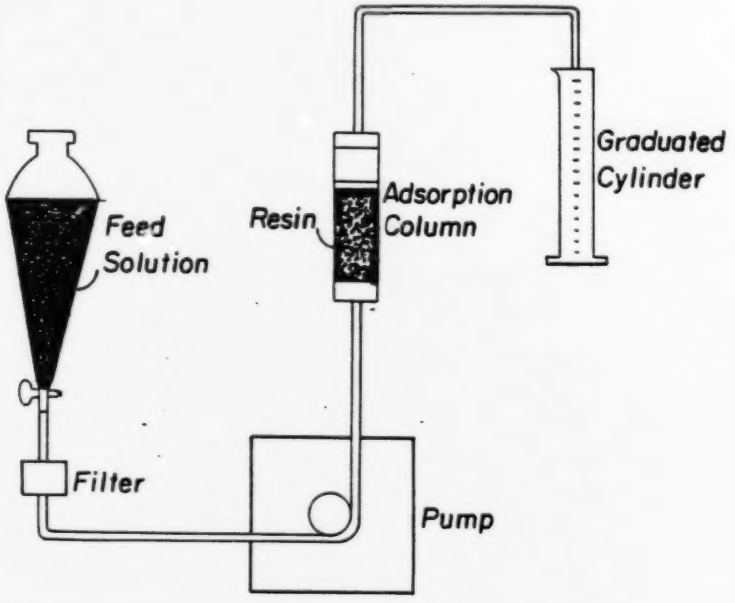

Fig. 6. Equipment set up for ion-exchange adsorption column.

where X^+ = ionic form of the resin. The highest gold recovery was achieved by the Bio-Rad AG50W-X16 with 98.6%, also extracting the highest amount of thiourea with 13.1%. However, this resin has produced the lowest gold loading. The best gold loading performance was achieved with the Bio-Rad AG50W-X8 but this has been overshadowed by its high facility to extract thiourea (the highest loading). This adsorption of thiourea by ion-exchange resins confirms the work of the U.S. Bureau of Mines (11). Species such as iron and copper are complexed with thiourea in solution and these complexes are adsorbed onto resin. Thiourea adsorption could then be explained by an exchange mechanism:

$$m\bar{X}^+ + M[TU]_n^{m^+} \rightleftharpoons mX^+ + \overline{M[TU]_n^{m^+}}$$

where $M[TU]_n^{m^+}$ = metal thiourea complex.

Table 7. Batch adsorption tests for the resins.
150 mL pregnant solution, 15 mL of resin, 60 minutes, 25°C

Resin	Recovery (%)			Loading (kg/t)		
	Au	Cu	Thiourea	Au	Cu	Thiourea
Dowex 50WX8	94.6	71.8	11.1	0.819	0.62	19.52
Dowex HCR-S	93.8	79.4	11.4	0.875	0.70	19.89
Dowex TG 650C	95.1	69.2	11.1	0.890	0.65	21.10
Dowex MSC-1	94.6	71.8	11.1	0.867	0.66	20.66
Bio-Rad AG50W-X8	97.9	86.8	11.9	0.978	0.93	30.73
Bio-Rad AG50W-X16	98.6	84.4	13.1	0.760	0.70	27.08
Bayer Lewatit OC1014	94.4	97.9	-2.5	0.953	1.07	-5.66

The Bayer resin, Lewatit OC1014 did not have the same problem of high thiourea adsorption and did provide a gold loading higher than the average (0.953 kg/t). In fact, the reason of the behavior of the Bayer resin with thiourea is the nature of the product. The Lewatit OC1014 is a thiourea resin and thus some thiourea is supplied to the solution during gold extraction. This explains the negative value of thiourea loading.

The better efficiency of macroporous resins to load gold compared with the normal cationic type was not observed in a straight-forward way. MSC-1 and Lewatit OC1014 are both macroporous resins but they do not appear to produce the better extraction. The Dowex HCR-S presents the lowest thiourea loading of the group of resins with a sulphonic active group and at the same time an interesting gold loading. Preliminary tests have shown that thiourea loading on the resin is a function of its concentration in solution. In fact in the same experimental conditions, thiourea loading onto HCR-S was decreasing by 5 kg/t if the initial thiourea concentration decreases from 8 g/L to 5 g/L.

Figure 7 shows the effect of the flow rate on equilibrium loading of gold onto the Dowex HCR-S at room temperature with a bottom flow ion exchange column. The decrease in the flow rate creates an increase in the gold loading. Plots 1 and 2 show the isotherms at 12 and 6 bed volumes/h result in respective maximum gold loading of 15.9 kg/t (7.0 g/L) and 22.6 kg/t (10.0 g/L) after being treated with 279 and 477 bed volumes of solution (Table 8). The adsorption at 3 bed volumes/h (plot 3) provides a maximum gold loading of 27.4 kg/t (12.1 g/L) after the treatment of the ion-exchanger with 675 bed volumes of pregnant solution. Analyses of the

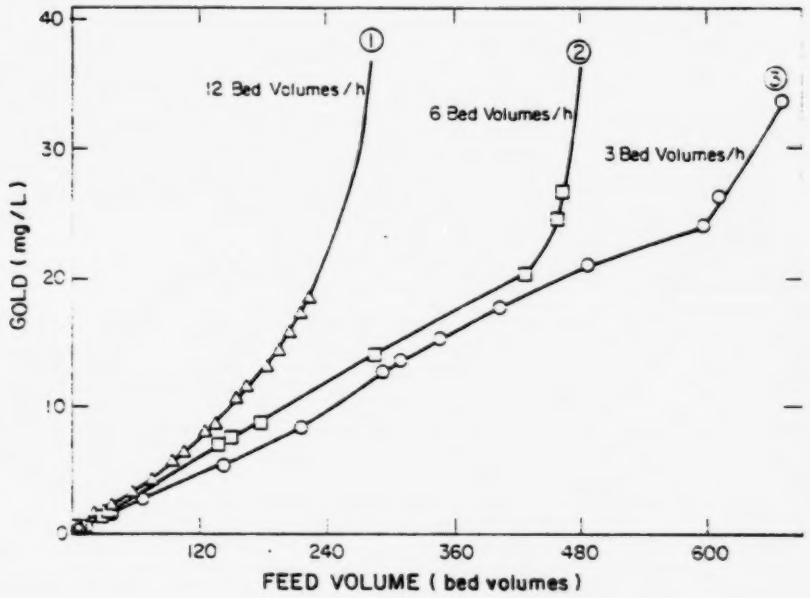

Fig. 7. Effect of the flow rate on equilibrium loading of gold onto strong acid cationic exchanger (HCR-S). Feed: 31 mg Au/L, room temperature.

resin by fire assay are providing results that confirm calculated loadings obtained by difference in head and effluent analysis. Figure 8 shows the gold loading onto HCR-S resin as a function of the gold in the effluent. A 95% extraction of gold (~1.6 mg/L in the effluent) results in a loading of 2.8 kg Au/t at a flow rate of 6 bed volumes/h and 1.3 kg/t Au at 12 bed volumes/h. Higher loading will create lower extractions. These gold loadings then are lower than previous work (13) and are related to thiourea concentration in the pregnant solution and also to competing ions. Higher thiourea concentration decreases the loading capacity of exchangers (11). Competing ions in large concentrations such as iron and arsenic reduce the amount of sites available in the ion exchanger.

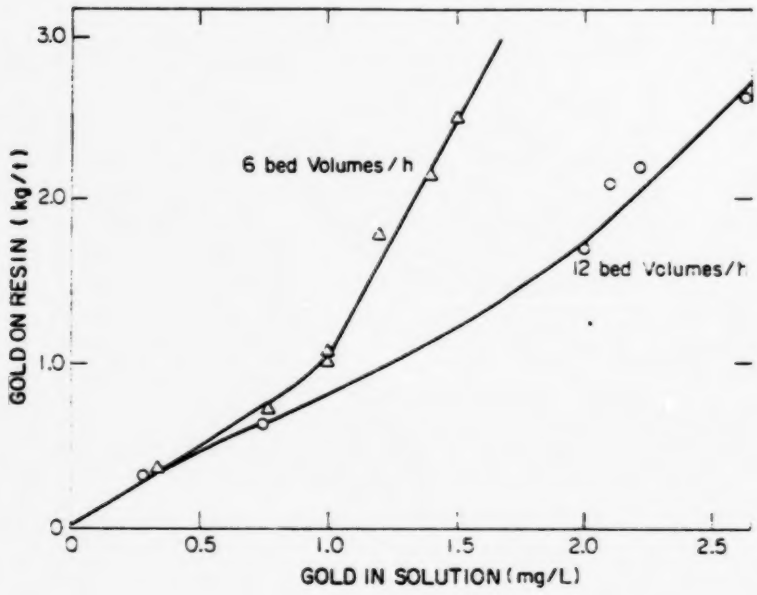

Fig. 8. Effect of the flow rate on equilibrium loading of gold onto strong acid cationic exchanger (HCR-S). Feed: 31 mg Au/L, room temperature.

To optimize the resin inventory, lower extraction can be used providing a higher gold loading. In fact, at 6 bed volumes/h, a gold loading of 5 kg/t will result in about 90% extraction of gold. The gold remaining in solution is not really a problem because of the obligation to recycle the leach liquor to render the process economical.

The selectivity of the strong acidic cationic resin HCR-S can be seen in Fig. 9. We were able to compare the three elements, gold, copper and antimony because of their comparable concentration in the solution (30-40 mg/L). According to the data, the exchanger has more selectivity for gold than copper and antimony. However, copper has more facility than antimony to be loaded on the ion-exchanger. The selectivity of a resin for one ion over another is largely a function of the size of the ion. The literature (25) presents the copper thiourea complex as a complex four, i.e.

$Cu[SC(NH_2)_2]_4^{2+}$. This copper thiourea complex could be bigger than the gold thiourea complex and it is less adsorbed into the resin. According to these results, antimony could also be bigger than the gold thiourea ionic complex. So far, no information on antimony thiourea complex is available in the literature. The copper loading at equilibrium is about three times less than the gold loading (Table 8). In spite of the fact that iron concentration in the feed is 250 times the gold concentration, iron loading on the resin is not more than two times higher than gold loading. These facts also show the selectivity of the resin.

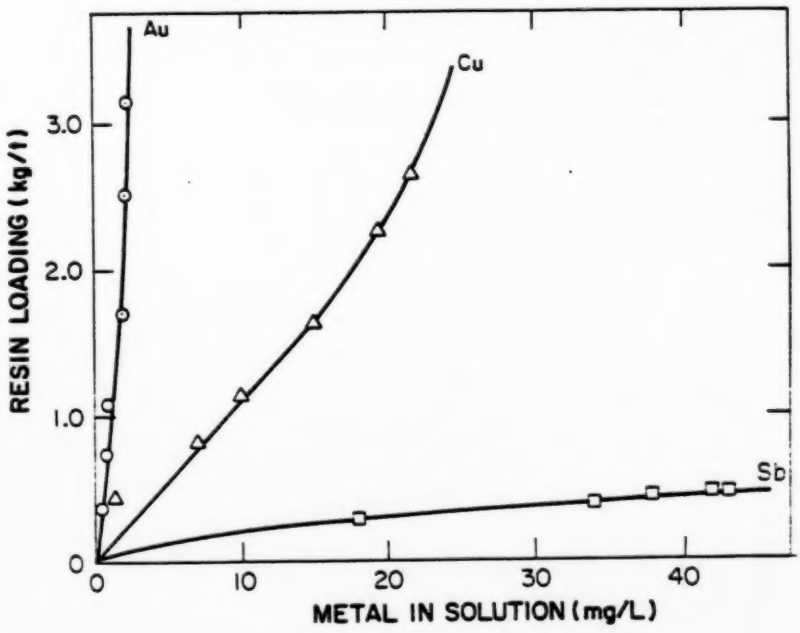

Fig. 9. Equilibrium loading of some metals onto a strong acid cationic ion exchanger (HCR-S). 12 bed volumes/h, room temperature.

Table 8. Equilibrium loading during column ion exchange adsorption test. HCR-S resin, room temperature. Feed: thiourea, 8.2 g/L, 33 mg Au/L, 40 mg Cu/L, 8.5 g Fe/L.

Flow rate (bed volumes/h)	Loading (kg/t) Au	Fe	Cu	Thiourea
3	27.4	49.9	9.2	46.0
6	22.6	41.0	7.6	38.2
12	15.9	32.8	5.9	17.8

Equilibrium loading of the resin, after being reached, with base metals such as iron can be modified. In fact, the resin continues to load gold but some of the loaded iron can be eluted by the thiourea solution at the same time. Iron loading is then changing with time, oscillating around a certain value. The evaluation of base metals content is then more simple and accurate by fire assay.

Figure 10 shows the breakthrough curves for thiourea and iron during loading of the HCR-S at 3 bed volumes/h and 12 bed volumes/h. Values at 6 bed volumes/h are not illustrated but are intermediate. Maximum loading

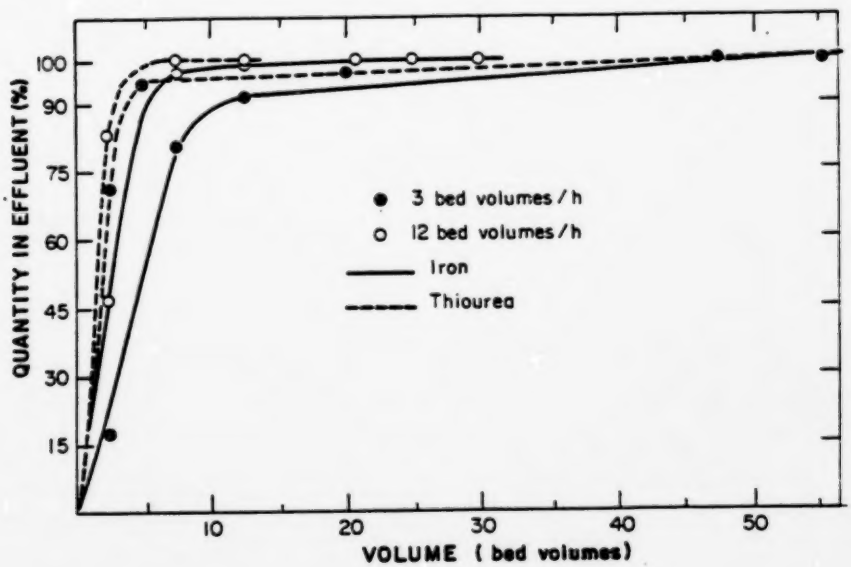

Fig. 10. Breakthrough curves for iron and thiourea function of the flow rate. Dowex HCR-S, room temperature.

increases with the decrease of flow rate. Thiourea loading reaches equilibrium at 17.8 kg/t after 7-8 bed volumes with a flow rate of 12 bed volumes/h. This equilibrium is obtained at 46.0 kg thiourea/t after 47 bed volumes with a flow rate of 3 bed volumes/h. In spite of its comparable concentration, iron reaches equilibrium after thiourea and provides higher loading onto the resin. In fact, about 32.8 kg iron/t were adsorped with a flow rate of 12 bed volumes/h increasing at about 50 kg iron/t at 3 bed volumes/h (Table 8). The equilibrium points were obtained at 20 bed volumes for the highest flow rate and at 50 bed volumes for the lowest one. Arsenic loading remains at lower values, representing 5 kg/t at 12 bed volumes/h.

Composition of the solution is the most important aspect for gold loading of a specific ion exchanger. Thiourea concentration, competing ions and also gold content will decide the equilibrium. In spite of the high concentrations of iron, thiourea and arsenic, the resin continues to load the gold thiourea complex after apparent saturation of these competing contaminants. Strong acid cationic ion exchanger shows a good selectivity for this gold thiourea complex. Base metals concentration such as iron and copper affect this equilibrium loading by a competing mechanism. Maximum equilibrium loading could be reduced to half its value as reported by Becker et al. (17) when the iron concentration increases. High gold loadings such as 20 g/L of resin can be obtained with a pregnant solution containing 1 g/L of gold but difficult to reach with the present feed, having significant concentration of base metals and only 30-40 mg Au/L.

Additional tests will show the relative selectivity of these resins and will indicate the further orientation of the research.

Gold Elution

Gold desorption from the ion exchange resins was investigated with some eluants. These are sodium thiosulphate, HCl-Br, cyanide solution and acidic thiourea solutions. Table 9 shows the batch test results on 15 mL of resin (Dowex HCR-5, Bio-Rad AG50W-X8, Bio-Rad AG50W-X16 and Bayer Lewatit OC1014) contacted with 50 mL of eluant for 2 hours at room temperature.

Table 9. Batch elution tests for some resins
50 mL eluant, 15 mL resin, 120 minutes, room temperature.

Eluant \ resin	Gold elution (%)			
	HCR-S	AG50W-X8	AG50W-X16	Lewatit OC1014
$Na_2S_2O_3$ 5%, pH=9	73.6	85.0	18.4	12.6
HCl 4N - Br 2%	23.7	40.6	33.6	2.0
NaCN 0.2 M-NaOH 0.2 M	2.6	9.5	2.0	4.1
HCl 4N-Thiourea 1%	8.3	5.5	2.8	2.0
H_2SO_4 0.5N-thiourea 10%	1.4	1.8	1.9	9.1

Sodium thiosulphate, 5% solution at pH 9 gives the best performance with 85% of elution of gold on the resin AG50W-X8. Gold stripping of the HCR-S shows also a good result with 74% but treatment of AG50W-X16 and Lewatit OC1014 resulted in elution below 20%. The mixture HCl 4N - Br 2% was found to elute with some efficiency on Dowex HCR-S and Bio-Rad resins but gave poor results on the Bayer resin. Acidic thiourea solutions reported in the literature to have some efficiency (2) or good efficiency (13,18) were not as suitable in these tests as well as the cyanide solution reported previously to elute gold from the cationic Bio-Rad AG50W-X8 with success (11).

A second elution contact of resins, in the same conditions, is shown in Table 10.

Table 10. Batch elution tests for resin, second contact, 50 mL eluant, 15 mL resin, 120 minutes, room temperature.

Eluant \ resin	Cumulative elution of gold (%)			
	HCR-S	AG50W-X8	AG50W-X16	Lewatit OC1014
$Na_2S_2O_3$ 5%, pH=9	97.0	90.9	34.9	21.6
HCl 4N - Br 2%	-	59.1	60.6	3.9
NaCN 0.2 M-NaOH 0.2 M	-	11.3	4.9	6.1
H_2SO_4 0.5N-thiourea 10%	3.2	3.6	3.7	16.8

The highest elution of gold was found to be 97% with the 5% solution of sodium thiosulphate at pH 9 on the HCR-S resin. Maximum elution achieved by the HCl-Br eluant was about 60% on Bio-Rad resins. The effect of sodium

cyanide did not show great promise. However, when the AG50W-X8 resin was previously contacted with a solution of HCl-thiourea, further gold elution with the solution NaCN 0.2 M-NaOH 0.2M has produced an extraction of gold up to 90% with few bed volumes. Thus, contacting the resin with an acidic thiourea solution provides successful elution of gold with a cyanide solution. The first treatment could be considered as a conditioning step; the acidic influent taking off base metal complexes. The cyanide solution is efficient because less species remain to complex with cyanide and the elution is less dependant on cyanide concentration.

Elution with thiourea thus appears to be a function of the acidity of the solution and also a function of thiourea concentration. So far, HCR-S and Lewatit OC1014 show the easiest elution with this liquor. It is possible that the increase of acid concentration as mentioned in the literature (2) and thiourea concentration would improve this step. We have not performed stripping tests with 6M $HCl/NaClO_2$ mentioned in the literature (17), as an efficient eluant because of the chlorine formation and the high reagent cost resulting in the stripping and conditioning steps using this eluant.

We have analysed the effect of thiosulfate solution to see if this eluant could have some fouling effect on a strong acid cationic exchanger. Previous results show no drastic decrease in the loading capacity of the resin or in the efficiency of the stripping.

The use of strong acid cationic resins is more promising than activated carbon in thiourea solutions. The ion exchanger does not provide the high loss of thiourea during the loading that occurs with activated carbon. The cationic resin also shows a better selectivity than activated carbon. Further tests will decide on the choice of resin(s) and eluant(s) for the gold recovery. The continuous electrolytic recovery of gold in the elution cycle (electroelution) accelerates removal of the gold from the ion exchange resin (26,27). We will consider the electroelution for its advantage and also for the completeness of the gold extraction.

The loss of resin during the RIP (resin-in-pulp) process is unknown. Studies on the physical attrition in the extraction stages and on osmotic cracking during elution and regeneration will provide values on these factors.

6. SOLVENT EXTRACTION

EXPERIMENTAL

Batch "shake out" tests were conducted on some organic extractants with an aqueous organic ratio of one. These organic extractants are: 8-hydroxyquinoline derivative (LIX 26, Kelex 100), isodecanol, tri-octyl methylammonium chloride (Aliquat 336), tri-oclylamine (Alamine 336), tri-isooctylamine (Adogen 381), tributyl phosphate (TBP) di-2-ethyl hexyl phosphoric acid (D2EHPA), mono-2-ethylhexyl phosphoric acid (M2EHPA), di-2,4,4-trimethylpentyl phosphinic acid (Cyanex 272), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A: Daihachi, SME 4'8: Shell), tri-octyl phosphine oxide (TOPO) and methyl-isobutyl ketone (MIBK). After being separated, organic and aqueous phases were sampled to be analysed by AAS.

Stripping tests were performed with HCl, citric acid, sodium tartarate, NH_4HF_2 and water. Stripping isotherms were established with the most promising aqueous media at room temperature.

RESULTS AND DISCUSSION

In the first batch of "shake out" tests, 9 organic extractants were tried. These were: 1) LIX 26 10% - isodecanol 10%, 2) isodecanol 100%, 3) TBP 50%, 4) Kelex 100 5% - isodecanol 5%, 5) Aliquot 336 5% - TBP 5%, 6) Alamine 336 0.05M - isodecanol 0.05M, 7) Adogen 381 5%, 8) D2EHPA 15% - TBP 5% and 9) MIBK 100%. The most promising extractants were Aliquot 336 5% - TBP 5% and D2EHPA 5% - TBP 5%; the former gave however phase precipitation in the organic. The other tests provide poor gold extraction, or formation or precipitates or were totally inefficient like MIBK 100%.

In the second batch of "shake out" tests, different concentrations of D2EHPA and TBP were tried. Other forms of phosphorus acids, i.e. phosphonic and phosphinic, were studied. Additional tests with Aliquot 336 and MIBK were performed to improve the gold extraction. Table 10 shows these tests.

With 10% TBP, the increase of D2EHPA concentration from 25% to 60% improves the extraction from 46.6% to 77.1%. The use of M2EHPA with TBP 10% slightly decreases the gold recovery. Phosphonic acid (PC-88A and SME 418) and phosphinic acid (Cyanex 272) resulted in a substantial decrease in extraction of gold. Precipitation often occurred in the aqueous phase or in

the organic phase during these tests. Only high concentration of TBP alone, i.e. 100%, shows efficiency in the gold extraction with 61.9% but the precipitation causes a problem.

The addition of D2EHPA 15% in TBP 50% improves the gold extraction to 77.4%, however, the precipitation still occurs with 50% of TBP (Table 11). Tests with Aliquat 336 - TBP or Aliquat 336 - TOPO or MIBK with D2EHPA did not show better performance in the gold recovery, and precipitation also resulted.

Kinetic tests for the extraction of gold by D2EHPA 40% - TBP 10% have shown that the equilibrium is reached in less than 10 seconds (see Table 12). The extension of the contact time of the organic with the aqueous phase causes an increase of iron extraction. If the contact time is less than 5 minutes, iron concentration in the organic could be kept below 200 mg/L with an A/O of 2. The increase of the temperature decreased the gold extraction but increased the iron recovery as can be seen in Table 13.

Table 11. Screening of extractants for the recovery of gold from thiourea solution. Feed: 41 mg Au/L, phase ratio A/O = 1.

Reagents	Gold extraction (%)	Remarks
D2EHPA 25% - TBP 10%	47.6	organic slightly hazy
D2EHPA 40% - TBP 10%	73.8	organic hazy
D2EHPA 60% - TBP 10%	77.1	organic slightly hazy
M2EHPA 40% - TBP 10%	67.1	organic slightly hazy
SME 418 40% - TBP 10%	17.6	aqueous cloudy, organic slightly hazy
PC-88A 40% - TBP 10%	23.5	aqueous cloudy, organic slighly hazy
Cyanex 272 40% - TBP 10%	11.8	organic milky
TBP 50% (in Varsol 140)	5.2	both phases cloudy
TBP 75% (in Solvesso 150)	7.3	both phases cloudy
TBP 100%	61.9	organic milky
TBP 50% - D2EHPA 15%	71.4	white precipitate in organic
Aliquot 336 10% - TBP 10%	50.0	-
Aliquot 336 5% - TOPO 5%	26.2	precipitates at the interface
MIBK 85% - D2EHPA 15%	47.6	organic, milky and precipitates

Table 12. Kinetic extraction of gold from thiourea solution with D2EHPA 40% - TBP 10%. Feed: 33 mg Au/L, room temperature, phase ratio A/O = 2.

Test	Time (s)	Organic composition Au (mg/L)	Fe (mg/L)
1	10	32	86
2	30	32	100
3	60	33	110
4	120	32	140
5	180	33	150
6	300	33	180
7	360	31	500
8	720	30	830

Table 13. Effect of the temperature on the gold extraction with D2EHPA 40% - TBP 10%. 3 minutes contact time. Feed: 41 mg Au/L.

Phase Ratio A/O	Temperature (°C)	Extraction (%) Gold	Iron	Separation Time (s)
3/1	room	42.4	15.0	120
1/3	room	75.8	8.5	100
3/1	50	12.1	24.0	30
1/3	50	51.5	12.8	15

There is then no advantage to increasing the temperature of solvent extraction when using such reagents.

The equilibrium isotherm of the extractant D2EHPA 40% with TBP 10% is given in Fig. 11. Equilibrium data were obtained by changing the phase ratio A/O from 1/5 to 20/1. This figure shows that gold extraction with this system will require 4 stages to reduce the precious metal concentration from 43 mg/L to 5 mg/L with a phase ratio O/A of 1. Successive extractions of gold from thiourea solution are presented in the following table. Figure 12 shows the gold loading of the solvent is a function of the raffinate composition.

Table 14. Successive extractions of gold from thiourea solution with D2EHPA 40%, TBP 10%. A/O = 1, room temperature, contact time = 2 minutes. Feed: 41 mg Au/L, 9.02 g Fe/L and 22 mg Cu/L.

Contact	Organic phase composition (mg/L)			Extraction (%)
	Au	Fe	Cu	Au
1	28	130	<0.5	68
2	48	220	<0.5	49
3	61	320	<0.5	39
4	72	390	<0.5	27
5	84	490	<0.5	29
6	85	560	<0.5	2

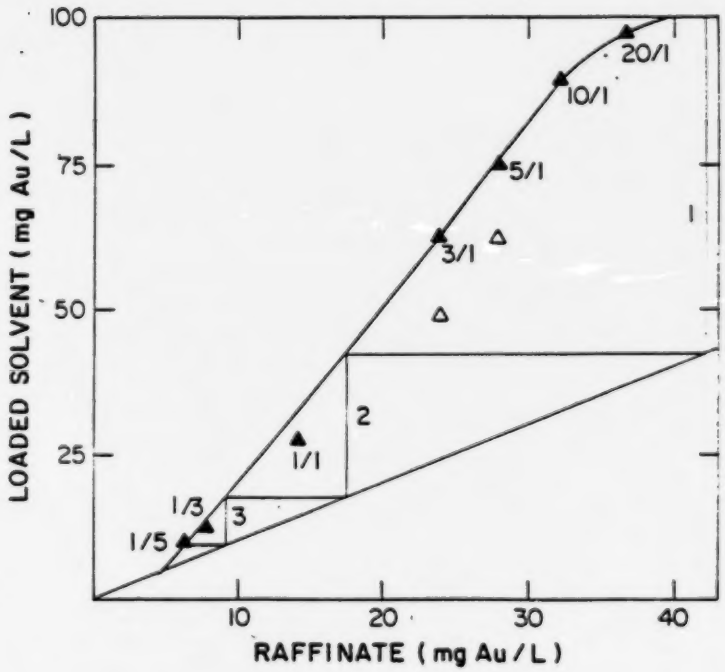

Fig. 11. Equilibrium isotherm for gold recovery with D2EHPA 40% - TBP 10%. Room temperature, feed: 43 mg Au/L.

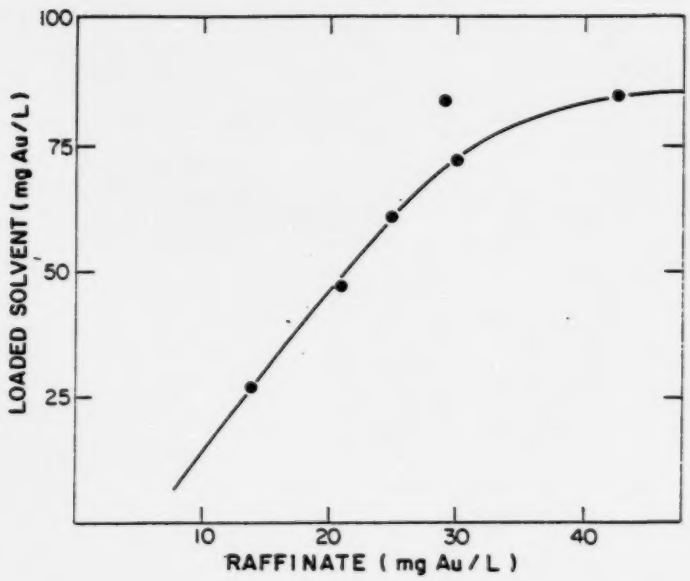

Fig. 12. Successive extraction of gold with D2EHPA 40% - TBP 10% in thiourea solution. A/O = 1, room temperature, 2 minutes. Feed: 41 mg Au/L.

The extraction with this solvent has some selectivity for gold. Most of the iron and the copper remain in the aqueous phase. Maximum loading of the organic appears to be around 85-90 mg Au/L. At the same time, the relative composition of iron and copper are respectively 560 mg/L and 0.5 mg/L. Iron and copper concentrations were then reduced by 16 times and 44 times while gold was concentrated by two times.

The following table shows tests performed to strip the gold from the organic.

Table 15. Screening of stripping solutions for gold from D2EHPA 40% - TBP 10%. O/A = 1, room temperature, 3 minutes, feed: 51 mg Au/L.

Reagents	Gold extraction (%)
Water	33
HCl 5%	62
HCl 10%	82
HCl 20%	84
HCl 30%	80
HCl 40%	67
Sodium tartarate 10%	-
NH_4HF_2 5%	-
Citric acid 10%	27

Hydrochloric acid provides the best gold stripping. Almost 85% of gold was been recovered with HCl 20% and of ratio O/A equal to 1. Citric acid 10% strips gold at 27% extraction but some precipitation occurs in the organic phase. Sodium tartarate 10% and NH_4HF_2 5% do not appear to efficiently remove the gold from the organic phase.

Optimum gold stripping with HCl occurs between 10% of acid and 20% of acid and is probably 85% with a phase ratio O/A = 1. However, the iron stripping increases with the increased acidity. There is therefore an advantage to strip gold at low acidity. The decrease of the phase ratio O/A to 1/10 has shown gold stripping of 98% with HCl 10%.

A room temperature stripping isotherm is shown in Fig. 13 for the removal of 86 mg Au/L from the loaded organic. A solution of HCl 10% readily strips the loaded solvent containing 86 mg Au/L to 4 mg Au/L in 4 stages with a phase ratio O/A of -3.16.

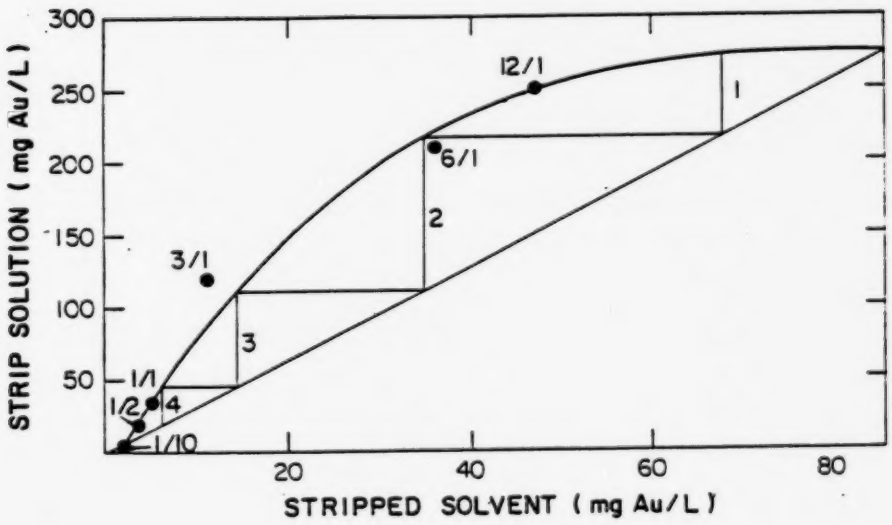

Fig. 13. Stripping isotherm for gold with HCl 10%. Contact time = 3 minutes, room temperature, feed: 86 mg Au/L.

Solvent extraction is showing selectivity for the recovery of gold from a thiourea solution. The stripping stage also provides an increase in the gold concentration, other ions remaining in the organic phase. Further tests are planned to investigate factors like pH, composition of the pregnant liqueur, thiourea consumption and solvent losses during the process.

7. CONCLUSIONS

Recovery of gold by aluminum cementation provides extraction up to 98%. However the precious metal content of the cement is poor (-2% gold) rendering the process uneconomical. Cementation with fine lead powder is totally inefficient in sulphuric media and the increase of the surface particle will increase the gold recovery but such practice is unattractive because of the decrease of precious metal content.

Activated carbon recovers gold from thiourea solution with 99% extraction. However, the extraction occurs with high loadings of thiourea which are poorly stripped from the carbon in presence of air. This process probably requires special equipment to recover the loaded thiourea.

Strong acid cationic ion exchange resins show selectivity to load the gold-thiourea complex in a solution containing iron, arsenic copper and antimony. Equilibrium loading is function of the solution composition. This selectivity will be the topic of further investigation with synthetic gold thiourea liquors.

Gold is not easily eluted from the strong acid cationic ion exchanger. Thiosulphate solution has shown so far the better performance to elute gold from a strong acid cationic ion exchange resin removing almost all gold with a limited volume of solution. Further studies will be required to optimize the elution of gold from the resins with thiourea solutions. Electroelution is planned to be the final step to recover gold from the effluent.

Solvent extraction of gold with D2EHPA 40% - TBP 10% has shown a selective extraction of gold from a thiourea solution. Effective stripping is possible with HCl 10% and selective stripping is a function of the acidity. Effect of the pH, composition of the pregnant liquor, thiourea lost and solvent losses have to be investigated in the future work. Pressure reduction, lead cementation and electrolysis will be evaluated as possible final recovery steps.

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